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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Corrosion Inhibitors

We, THE GEIGY COMPANY LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester 22, and formerly of 15, Norfolk Street, Manchester 2, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion inhibitors, and in particular more particularly to aqueous or other media containing such corrosion inhibitors for use in contact with metals.

It is well known that certain metals, when forming part of a system containing an aqueous medium such as, for example, a heat transfer system or a hydraulic power system, are susceptible to corrosion. This corrosion is accelerated when the temperature of aqueous medium is raised, as it may be, for instance, in the cooling system of an internal combustion engine. Furthermore, when freezing point depressants are added to such media, the composition obtained may be more corrosive than is a medium which does not contain these additives. Thus, an aqueous medium containing ethylene glycol which is commonly used in anti-freeze formulations is found to be more corrosive than is unmodified water towards certain metals or alloys used in the construction of water distribution systems, especially when such metals or alloys are present in juxtaposition, for example aluminium in contact with steel, or copper and steel soldered to brass. Where copper is present, it is known that it can promote oxidation of the glycol, thereby producing organic acids which may cause dissolution of copper by the medium and so induce self-accelerated corrosion. Any aluminium surfaces present may become pitted, or more extensively corroded, and ferrous alloys rapidly rusted.

A considerable amount of research has been directed to discovering ways of inhibiting the corrosion of metals by aqueous media. Among

additives that have been previously proposed for this purpose are sodium nitrite, borax, sodium nitrate and sodium benzoate in admixture and triethanolamine phosphate singly or in admixture with the sodium salt of 2-mercaptobenzthiazole. While these additives may provide some protection for ferrous alloys exposed to the corrosive effects of aqueous media, certain non-ferrous alloys, especially copper and aluminium alloys, may still be extensively corroded. Although sodium 2-mercaptobenzthiazole can inhibit corrosion of copper, the technical grade of this compound, as commonly used, is not readily soluble in aqueous media and shows a tendency to oxidise to a very insoluble disulphide.

In British Patent Specification No. 811,675, there is disclosed an anti-freeze composition comprising ethylene glycol and containing sodium 2-mercaptobenzthiazole in which the latter can advantageously be replaced wholly or in part by benzotriazole as a preventive for copper take-up. The compositions disclosed therein may optionally contain a small proportion of an additional corrosion inhibitor, for example, triethanolamine phosphate or sodium nitrite. When non-ferrous metals or alloys are present, however, these compounds, which are specific to ferrous materials, may actually induce corrosion and militate against the protective action of benzotriazole on non-ferrous metal components.

It is an object of the present invention to provide improved corrosion inhibitor compositions.

According to the present invention, a corrosion inhibitor composition comprises a mixture of benzotriazole and/or methylbenzotriazole and an alkali metal, ammonium, amine or alkanolamine salt of a saturated dicarboxylic acid having from six to thirty carbon atoms per molecule.

The present invention also comprises a process of protecting a metal or metal article susceptible to corrosion, which comprises con-

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tacting the metal or metal article with a composition comprising a mixture of benzotriazole and/or methylbenzotriazole and an alkali metal, ammonium, amine or alkanolamine salt of a saturated dicarboxylic acid having from six to thirty carbon atoms per molecule.

If the salt of the saturated dicarboxylic acid is an alkali metal salt, this may be for example a sodium or potassium salt. If the salt of the dicarboxylic acid is an amine salt, the amine moiety may be for example a straight- or branched-chain alkylamine; the amine may be a primary, secondary or tertiary amine. If the salt of the dicarboxylic acid is an alkanolamine salt, the alkanolamine moiety may be a mono-, di- or tri-alkanolamine, for example mono-, di- or tri-ethanolamine. The salt of the saturated dicarboxylic acid may be the dibasic salt, for instance the disodium, dipotassium or diammonium salt, in which both carboxylic acid groups in the molecule of the acid are neutralised by the corresponding base; or the salt may be the monobasic salt, for instance the monosodium, monopotassium or mono-ammonium salt, in which only one of the carboxylic acid groups in the molecule is neutralised by the base, the other being a free carboxylic acid group. If both carboxylic acid groups in the molecule are neutralised, each group may be neutralised by the same or different base to give a single or mixed salt, respectively.

The salt of the dicarboxylic acid is preferably the salt of a saturated aliphatic dicarboxylic acid having from six to twenty carbon atoms per molecule, for example adipic acid, suberic acid, azelaic acid, sebacic acid or 1:12-dodecanedioic acid. The dicarboxylic acid may be a single saturated dicarboxylic acid, or a mixture of two or more thereof, or as a mixture with other carboxylic acid or acids.

The corrosion inhibitor composition may, if desired, contain a minor proportion of borax, preferably a proportion within the range from 0.1% to 10% by weight based on the total weight of the composition.

The concentration of the benzotriazole and/or methylbenzotriazole present in the composition is preferably within the range of from 0.01% to 5% by weight based on the total weight of the composition. The concentration of the salt of the dicarboxylic acid is preferably within the range of from 0.1% to 5% by weight based on the total weight of the composition.

The corrosion inhibitor composition may, if desired, be diluted with water or an organic solvent, or with a mixture of water and an organic solvent, for example to provide an anti-freeze composition or other composition for use in a heat transfer system. The organic solvent may be an aliphatic alcohol, for example, methyl alcohol, ethyl alcohol, or other aliphatic monohydric alcohol; ethylene glycol or other alkylene glycol; or glycerol.

The amount of water or organic solvent, present may be varied to suit the purpose for which the composition is intended, and may also depend on the temperature at which the composition is to be employed and the period for which it is exposed to the atmosphere. In general, a satisfactory corrosion inhibiting effect is achieved by using a composition containing from one to four parts by weight of the diluent water and/or organic solvent per part by weight of the undiluted composition of the invention. The concentration of the benzotriazole and/or methylbenzotriazole in the diluted composition is preferably within the range of from 0.005% to 1% by weight, that of the salt of the dicarboxylic acid is preferably within the range of from 0.058 to 1%, and that of any borax present is preferably within the range of from 0.05% to 2% by weight, based in each case on the total weight of the diluted composition. If the composition is aqueous, the pH value is advantageously within the range of from 6.5 to 8.5.

The corrosion inhibitor composition may be produced by a process comprising admixing the benzotriazole and/or methyl benzotriazole with the salt of the saturated dicarboxylic acid. The benzotriazole or methyl benzotriazole may be added to an aqueous or other liquid medium in admixture with, or separately from, the salt of the dicarboxylic acid; instead of adding the actual salt to the medium, the appropriate saturated dicarboxylic acid and base may, if desired, be separately added to the medium so as to form the salt in the medium.

The compositions of the present invention may be used to inhibit the corrosion of non-ferrous metals and alloys containing non-ferrous metals, for example copper or an alloy of copper, for instance brass, or aluminium or an alloy of aluminium, and also to inhibit the corrosion of ferrous alloys.

Compositions of the present invention include those intended for use in heat transfer systems, such as cooling systems for internal combustion engines and heating installations in buildings and also systems applied in hydraulic engineering and in lubrication, whenever these systems contain copper or its alloys. The compositions include, for instance, anti-freeze composition, for use in the radiators of internal combustion vehicles, containing a glycol, for example ethylene glycol, as a major component.

The following Examples further illustrate the present invention.

EXAMPLE 1

This Example illustrates the superior corrosion inhibiting effect of a mixture of benzotriazole and the triethanolamine salt of sebacic acid, when compared with standard formulations described in the prior art.

To produce the type of system usually found in an internal combustion engine, com-

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liquids provided, with constant stirring (300 revolutions per minute), free access of air being permitted. Observations were then made on the weight change of the separate components and their general appearance as on that of the solutions. The results obtained are set out in Table I.

To each of seven wide-mouthed jars was added 200 millilitres of 25% volume/volume aqueous ethylene glycol. Six of the test solutions were then treated with corrosion inhibiting systems as indicated in the following Table I, the remaining specimen being used as a control. The composite metal loops to be tested were immersed for six months at a temperature of 20°C. in each of the seven

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posite metal loops were prepared containing elements of cold-rolled mild steel sheet (1/64th inch thickness), aluminium sheet-anodising quality (1/64th inch thickness) and pure copper foil. These components were bolted together with brass bolts to form a ring with all metals in contact. The total area of each of the assemblies was approximately 24 square inches, with a total weight of about 15 grams.

TABLE I

Composition	Inhibitor System volume/volume %	Weight Change (milligrams)			Appearance of Metal System after Test
		Copper	Aluminium	Steel	
A	0.05% Sodium 2-mercaptobenzthiazole 0.275% Phosphoric acid (specific gravity 1.75) Triethanolamine to pH 7.2	+2.7	+0.8	+42.1	Copper dull. Grey deposit on steel. Heavy sludge.
B	As above, with sodium 2-mercaptobenzthiazole omitted.	-52.7	+6.3	-42.3	Severe corrosion of all metals.
C	1.25% Sodium benzoate 0.12% Sodium nitrite	+13.1	+10.6	-0.4	Blue deposit on copper. Steel iridescent.
D	0.75% Borax	-2.2	-0.5	+1.2	Copper tarnished; copper in solution.
E	No. inhibitor pH 7.5	+0.1	+2.8	-600	Severe rusting
F	0.05% Benzotriazole 0.275% Phosphoric acid (specific gravity 1.75) 0.25% Cyclohexylamine Triethanolamine to pH 7.2	<-1.0	<-1.0	+9.8	Grey deposit on steel; solution discoloured.
Example 1	0.1% Benzotriazole 0.25% Sebacic acid Triethanolamine to pH 7.2	<-1.0	0	<-1.0	All metals and solution unchanged in appearance.

These results clearly indicate that the composition of the Example proved to be highly superior as a corrosion inhibitor, when tested against several formulations in an aqueous medium intended for use as a freezing depressant. Furthermore, the improvement shown when compared with a commercially-available anti-freeze composition containing benzotriazole in the absence of a saturated aliphatic dicarboxylic acid, is well brought out.

EXAMPLE 2
Composite metal loops, as described in Example 1, were heated in separate 300 millilitre-volumes of 25% volume/volume-aqueous ethylene glycol under reflux at a temperature of 103°C. for a combined period of 96 hours, intermittently during this period being allowed to stand immersed in the cold compositions for a total time of 276 hours. The results obtained are given in Table II.

TABLE II

Composition	Inhibitor System volume/volume %	Weight Change (milligrams)		Appearance of Metal System after Test
		Copper	Aluminium	
H	0.05% Sodium 2-mercaptopbenzthiazole 0.275% Phosphoric acid (specific gravity 1.75) Triethanolamine to pH 7.2	+2.4	-2.2	+71 Steel severely blackened; copper and aluminium blackened and tarnished; much sludge
I	0.125% Sodium nitrite 0.1% Benzotriazole 0.25% Cyclohexylamine	+3.5	+3.9	+10.6 Copper darkened; aluminium dull and covered with black deposit; steel iridescent
Example 2	0.1% Benzotriazole 0.25% Sebacic acid Triethanolamine to pH 7.2	+0.9	+1.6	+0.5 Copper slightly dulled; other metals unchanged

These rigorous tests serve to demonstrate that the composition of Example 2 exerts a greater corrosion-inhibiting effect, when used in an anti-freeze composition, than do the other formulations H and I used for the purpose of comparison. Moreover, although benzotriazole is an ingredient common to Composition I and the composition of Example 2, the enhanced anti-corrosive effects obtained by the conjoint use of benzotriazole and the alkylolamine salt of a saturated aliphatic dicarboxylic acid, are clearly apparent.

EXAMPLE 3

The composition of Example 1 and the comparative Comparison A were tested comparatively in an experimental rig containing aluminium, tinned brass, mild steel and cast iron and provided with facilities for heating and for the ingress of air at the rate of 5 millilitres per minute. After heating for 400 hours at about 80°C., Composition A was found to have heavily attacked all the metal components except the aluminium, with pronounced graphitisation of the cast iron. By contrast, the composition of Example 1 gave rise to only slight attack on the aluminium and no attack on the other three components.

EXAMPLE 4

A coolant for summer use in the radiators of road vehicles was formulated by dissolving 5 parts by weight of triethanolamine sebacate and 2 parts by weight of benzotriazole in

water and adjusting the pH value to 7.

This solution was diluted with sufficient water to fill the cooling system in use and composite metal loops, as described in Example 1, were suspended in the coolant composition, a series of similar metal loops being suspended in the unmodified water added to similar cooling systems. After treatment for five months, the metal loops in the treated systems were in excellent condition, apart from some blackening of the aluminium. These results were in marked contrast to those obtained on the untreated systems, in which the metal loops under test had disappeared completely. Moreover, no evidence of rusting was apparent in cases where the coolant composition was used; but substantial amounts of rust were obtained from the untreated systems.

Although the compositions in the above Examples 1 to 4 in accordance with the present invention contained benzotriazole, similar results could be obtained by using methylbenzotriazole instead of the benzotriazole in the compositions produced and tested in those Examples.

EXAMPLES 5 to 12

Composite metal loops, as described in Example 1, were heated in separate 300 millilitre volumes of 25% volume/volume aqueous ethylene glycol under reflux at 103°C. for 300 hours. The results obtained are given in Table III, together with those of a number of other formulations outside the present invention for comparison.

TABLE III

Composition	Inhibitor Formulation	Weight changes (milligrams) after cleaning			Appearance of metal specimens after test, before cleaning		
		Copper	Aluminium	steel	Copper	Aluminium	Steel
K	0.05% Sodium 2-mercaptobenzthiazole 0.257% Phosphoric acid (specific gravity 1.75)	-7.7	-7.1	-10.3	Tarnished	Blackened	Severely blackened
L	Triethanolamine to pH 7.2 1.5% Sodium Benzoate 0.125% Sodium Nitrite pH 7.0	-4.5	-1.1	-0.1	Tarnished	Surface dull	As original
M	0.75% Borax pH 8.0	-0.8	-167.7	+2.9	Slight tarnish	Heavy uniform etching	Slight blackening
N	0.125% Sodium nitrite 0.1% Benzotriazole 0.25 Cyclohexylamine	-1.2	-2.8	-17.5	Tarnished	Dull black deposit	Iridescent discolouration
Example 6	0.1% Benzotriazole 0.25% Sebacic acid 0.44% Triethanolamine pH 7.2	0.0	-0.1	-0.7	As original	As original	As original
Example 7	0.05% Benzotriazole 0.2% Sebacic acid 0.25% Borax 0.35% Triethanolamine pH 7.6	0.0	+0.4	-0.4	As original	Slight surface dulling	Slight darkening

TABLE III

Weight changes (milligrams) after cleaning Appearance of metal specimens after test, before cleaning

Composition	Inhibitor Formulation	Weight changes (milligrams) after cleaning			Appearance of metal specimens after test, before cleaning		
		Copper	Aluminium	steel	Copper	Aluminium	Steel
Example 8	0.05% Methyl benzotriazole 0.2% Sodium sebacate 0.25% Borax pH 7.8	-0.2	+0.4	-1.0	Slight tarnish	Dark grey surface	Slight darkening
Example 9	0.05% Methyl benzotriazole 0.2% Ammonium sebacate 0.25 Borax pH 7.2	+0.8	+1.7	+0.1	Slight tarnish	Coloured Sheen on surface	As original
Example 10	0.05% Benzotriazole 0.15% Adipic acid 0.25% Borax 0.35% Triethanolamine pH 7.6	-0.1	+1.3	-3.6	Slight tarnish	Slight dulling	Slight edge tarnish
Example 11	0.05% Benzotriazole 0.19% Azelaic acid 0.25% Borax 0.35% Triethanolamine pH 7.6	-0.6	-0.3	-1.0	Slight tarnish	Slight dulling	As original
Example 12	0.05% Benzotriazole 0.23% 1:12-Dodecanedioic acid 0.25% Borax 0.35% Triethanolamine pH 7.6	0.0	-0.8	-1.4	As original	Slight dulling	Slight darkening

WHAT WE CLAIM IS:—

1. A corrosion inhibitor composition which comprises a mixture of benzotriazole and/or methylbenzotriazole and an alkali metal, ammonium, amine or alkanolamine salt of a saturated dicarboxylic acid having from six to thirty carbon atoms per molecule. 5
2. A composition claimed in Claim 1 wherein the dicarboxylic acid is a saturated aliphatic dicarboxylic acid having from six to twenty carbon atoms per molecule, or a mixture of two or more thereof. 10
3. A composition claimed in Claim 2 wherein the dicarboxylic acid is adipic acid, suberic acid, azelaic acid, sebacic acid or 1:12-decanedioic acid. 15
4. A composition claimed in any of the preceding Claims wherein the composition contains from 0.1% to 10% by weight of borax based on the total weight of the composition. 20
5. A composition claimed in any of the preceding Claims wherein the concentration of the benzotriazole and/or methylbenzotriazole is within the range of from 0.01% to 5% by weight based on the total weight of the composition. 25
6. A composition claimed in any of the preceding Claims wherein the concentration of the salt of the dicarboxylic acid is within the range of from 0.1% to 5% by weight based on the total weight of the composition. 30
7. A composition claimed in any of the preceding Claims diluted with water and/or an organic solvent. 35
8. A composition claimed in Claim 7 wherein the organic solvent is methyl alcohol, ethyl alcohol, ethylene glycol, glycerol or other aliphatic alcohol. 40
9. A composition claimed in either of Claims 7 and 8 containing from one to four parts by weight of the diluent water and/or organic solvent per part by weight of the undiluted composition. 45
10. A composition claimed in Claim 9 wherein the concentration of the benzotriazole and/or methylbenzotriazole is within the range of from 0.005% to 1% by weight based on the total weight of the composition.
11. A composition claimed in either of Claims 9 and 10 wherein the concentration of the salt of the dicarboxylic acid is within the range of from 0.05% to 1% by weight based on the total weight of the composition. 50
12. A composition claimed in any of Claims 9 to 11 wherein the composition contains borax in a concentration within the range of from 0.05% to 2% by weight based on the total weight of the composition. 55
13. An aqueous composition claimed in any of Claims 9 to 12 wherein the pH value of the composition is within the range of from 6.5 to 8.5. 60
14. A composition claimed in Claims 1 or 7 and substantially as described in any of the Examples. 65
15. A process of producing a composition claimed in any of the preceding Claims which comprises admixing the benzotriazole and/or methylbenzotriazole with the salt of the dicarboxylic acid. 70
16. A process of producing a composition claimed in any of Claims 1 to 14 which comprises adding the benzotriazole and/or methylbenzotriazole to an aqueous or other liquid medium, the appropriate saturated dicarboxylic acid and base being added separately to the medium so as to form the salt in the medium. 75
17. A process of producing a composition claimed in any of Claims 1 to 14 substantially as described in any of the Examples. 80
18. A process of protecting a metal or metal article susceptible to corrosion which comprises contacting the metal or metal article with a composition claimed in any of the preceding Claims. 85
19. A process of protecting a metal or metal article claimed in Claim 18 wherein the metal, or metal of the article, is copper, aluminium, or an alloy of copper or of aluminium.

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